

THE STEREOSELECTIVE CONVERSION OF VINYSILANES TO γ -SUBSTITUTED ALLYLSILANES VIA HIGHER ORDER CUPRATES

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Abstract: Pure *cis*-vinylsilanes are efficiently converted to *cis*-epoxysilanes which react smoothly with $\text{Li}_2\text{Cu}(\text{CN})(\text{CH}_2\text{TMS})_2$ to provide the corresponding erythro disilylated alcohol, in excellent yield and isomeric purity. Elimination of the elements of TMSOH affords either the pure *cis*- or *trans*- γ -substituted allylsilanes, under basic or acidic conditions, respectively.

The chemistry of allylsilanes has provided synthetic organic chemists with a multitude of new selective carbon-carbon forming reactions.² The methods used for the preparation of regio- and stereo- defined allylsilanes are expanding in a parallel fashion, reflective of their increasing importance as reagents in organic synthesis.³ Our interest in these compounds was stimulated by the fact that no method for the conversion of stereodefined vinylsilanes to their corresponding allylic homologues was available. We felt that such a conversion would constitute an important addition to the synthetic versatility of organosilanes in a general sense. Operationally-simple procedures were sought which would involve organosilane intermediates of established synthetic value. It was considered essential that the approach be capable of producing either the *cis* or the *trans* allylsilanes in high isomeric and chemical purity with a wide range of substituents at the *gamma* position of the allylsilane. Our reaction sequence is outlined in Scheme 1.

SCHEME 1

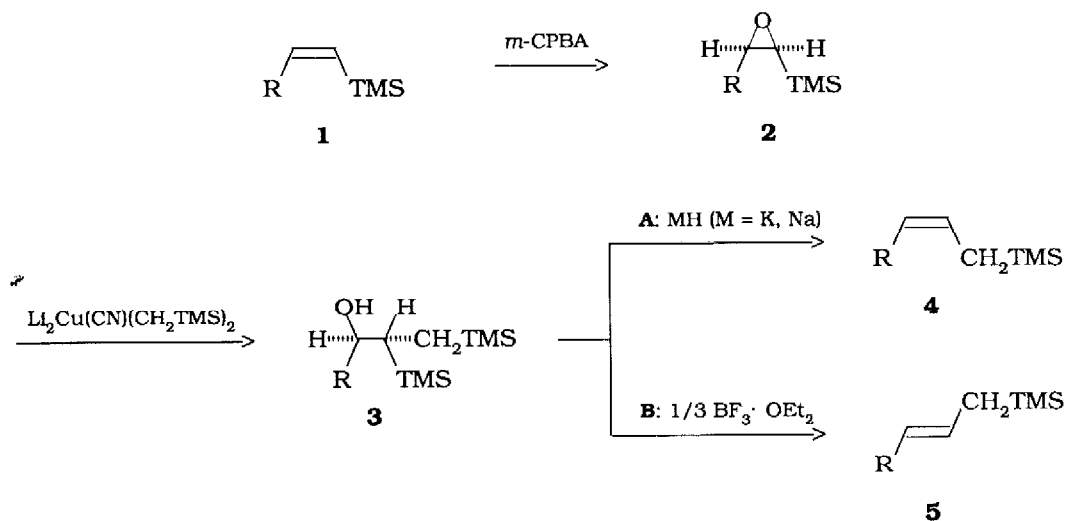


Table 1. Conversion of *cis*-Vinylsilanes to Allylsilanes.

compd	R	% yield for step ^a			
		2	3	4	5
1a	Me	88	90 ^b	92	99
1b	<i>n</i> -Pr	80	86 ^b	96	99
1c	<i>n</i> -Bu	84	91 ^b	98(85)	93(92)
1d	<i>t</i> -Pr	82	81 ^c	97	96
1e	<i>t</i> -Bu	80	90 ^c	99	91
1f	Ph	76	89 ^c	91 ^d	96

^a Isolated product yields (>99% chemical and isomeric purity) except for **4** and **5** which were determined by GC employing a hydrocarbon internal standard. In all cases, excepting **5f** (98% *E*), the products were formed in >99% isomeric purities and were isolated in pure form by distillation. Standard preparative procedures for **4c** and **5c** to give distilled products resulted in the yields given in parentheses. ^b Conditions: 6 h, 0°, THF. ^c Conditions: 7 h, 25°, EE. ^d NaH (LAH-treated⁴) was employed in this case (15 min, reflux, DME).

Available from the hydroboration/protonolysis of silylacetylenes,⁵ the conversion of the *cis*-vinylsilanes (**1**) into the corresponding epoxysilanes (**2**) was accomplished in the standard manner with *m*-chloroperbenzoic acid in methylene chloride. To avoid side reactions and to maintain the pure (>99%) *cis* product geometry, the following procedure is representative.

To a stirred solution of *m*-chloroperbenzoic acid (9.7 g (80%); 45 mmol) in methylene chloride (100 mL) at 0°C was added the *cis*-vinylsilane (30 mmol) dropwise. The ice bath was removed and, after 2 h at 25°C, the mixture was filtered and the solid acid was washed with CH₂Cl₂ (20 mL) and the filtrate was extracted with saturated K₂CO₃ solution (3 x 30 mL), dried with anhydrous K₂CO₃, concentrated and distilled to afford the desired epoxysilane (**2**).

As a representative silyl epoxide, the ring-opening reaction of *cis*-1-trimethylsilylpent-1-ene oxide (**2b**) was examined with the organocuprates derived from TMSCH₂MgCl/CuI (10%)⁶ and TMSCH₂Li/CuI (2:1).⁷ The former process led to a product mixture of starting material, the desired disilyl alcohol (**3b**), allylsilane (**4b**) and other unidentified products. In the latter case, after 12 h at 0°C, only 10% reaction of **2b** had reacted giving the desired alcohol, **3b**. These problems were overcome employing a 2:1 ratio of TMSCH₂Li and CuCN to give the corresponding higher order cuprate (Lipshutz reagent)⁸ which reacted cleanly with **2b** in 6 h at 0°C to give the desired *erythro* disilylated alcohol (**3b**) in 86% yield. This representative procedure is described below. For the more hindered systems (*i.e.* **3d-f**), the best results were obtained at 25°C in ether solvent (*cf.* Table 1).

To CuCN (1.79 g; 20 mmol) in THF (50 mL) at -78°C was added trimethylsilylmethylolithium in hexanes (44.6 mL 0.87 M; 40 mmol) dropwise. The cold bath was removed and dissolution occurred after ca. 15 min. at which time the mixture was recooled to -78°C and the epoxide (20 mmol) was added dropwise *via* syringe. After slowly warming to 0°C , the mixture was allowed to stir for an additional 6 h. The reaction was quenched with a 9:1 NH_4Cl (sat.)/ NH_4OH (conc.) solution (50 mL). After stirring for 15 min., extraction with ether (50 mL) gave an organic layer which was dried (Na_2SO_4), concentrated and distilled to give the desired *erythro* disilylated alcohol, **3**.

The discovery of Hudrlik⁹ that β -hydroxysilanes undergo *syn*-elimination with bases such as KH or KOBu^t and *anti*-elimination with both Lewis and Bronsted acids led to a stereospecific synthesis of either *cis* or *trans* alkenes depending upon the diastereomeric alcohol selected for the process. For our system this elimination would lead to allylsilanes, compounds which themselves are sensitive to both acids and bases. Thus, the elimination of the elements of TMSOH was investigated under both basic and acidic conditions with modified procedures aimed at maximizing the yield of the desired allylsilane products. For the *syn* (basic) eliminations, KH was particularly effective, producing **4** with >99% stereoselectivity. Only in the case of **3f**, did we observe desilylation (*i.e.* 1-propenylbenzene (60:40 *c/t*) with KH. This problem was overcome using NaH in DME (15 min, reflux) which gave **4f** cleanly. For the *anti* eliminations, we find that, in the case of BF_3 etherate, only 1/3 mole of the reagent is required per silylated alcohol to effect the complete elimination with >99% stereoselectivity in high yield. Only **5f** (R = *t*-Bu), is formed with a significant amount of the *cis* isomer (ca. 2% **4f**). We hasten to point out that our results are significantly better than those previously reported for the elimination of TMSOH from **3**, prepared from an alternative route.¹⁰ This suggests that either this route did not consistently give **3** in isomerically-pure form or the conditions employed for the eliminations were not optimal. We found the following procedures to give excellent results.

Commercial 35% KH in mineral oil (1.14 g) was washed with pentane (3x15 mL) and dried under a stream of nitrogen. To this was added THF (20 mL) and to the stirred slurry was added **3c** (2.6 g; 10 mmol), *via* syringe, dropwise. After 1 h at 30°C , the mixture was centrifuged and the decanted solution was poured into a separatory funnel containing a mixture of saturated NH_4Cl (50 mL) and ether (50 mL). After separation, the organic material was dried (K_2CO_3), concentrated *in vacuo* and distilled at 55 Torr to give 1.45 g (85%) of **4c**, bp 88°C . Other examples were examined under similar conditions and, with added internal standard, analyzed by capillary GC. Concentration and distillation gave a pure sample of the *cis*-allylsilane for spectroscopic and analytical data. From the pure sample, a correction factor was determined in each case from which the GC yield was calculated (*cf.* Table 1).

To a stirred solution of **3c** (2.6 g; 10 mmol) in CH_2Cl_2 (20 mL) at 0°C was added boron trifluoride etherate (0.47 g; 3.3 mmol), dropwise. After 15 min., the solution was poured into a separatory funnel containing a mixture of saturated NaHCO_3 (50 mL) and ether (50 mL). After separation, the organic material was washed with saturated NaHCO_3 (2x50 mL), dried (K_2CO_3), concentrated *in vacuo* and distilled at 55 Torr to give 1.57 g (92%) of **5c**, bp 88°C . See above for the GC yield determinations.

In this study, we report a new, general method for the conversion of pure *cis*-vinylsilanes to either the corresponding *cis*- or *trans*- γ -substituted allylsilanes. Through the stereoselective ring-opening of silyl epoxides with subsequent Hudrlik eliminations, the stereochemical control of the process is rigorously maintained. The epoxysilane approach also is well-suited for the precise control of the regiochemistry, a problem of other methods.¹⁰ With these develop-

ments, the conversion of stereodefined vinylsilanes to their homologated allylic counterparts can be accomplished in a convenient, highly selective, and efficient manner.

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